



Silylated hydrophobic zeolites with enhanced tolerance to hot liquid water



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ABSTRACT

Untreated USY zeolites have low tolerance to hot liquid water, which makes them unsuitable for upgrading of biomass-derived liquid compounds in biphasic systems. However, the stability of USY zeolites can be greatly improved by functionalizing their external surface with organosilanes. Here, the structural stability of a commercial H-USY zeolite (Si/Al = 30) in the presence of hot liquid water has been investigated after functionalization with organosilanes of varying alkyl chain length (C2–C18). The structural tolerance of various samples to liquid water has been compared upon exposure to reaction conditions in water/oil emulsions at 200 °C. In another set of experiments, structural changes have been monitored after exposure to increasing partial pressures of pure water vapor until a liquid phase is formed. The losses in crystallinity, surface area, and microporosity have been quantified by N₂ physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and infrared spectroscopy (DRIFTS). It is shown that the rate of collapse of the crystalline structure is not determined by the chemical potential of the water molecule inside the zeolite, but rather by the presence of a liquid aqueous phase, which favors dissolution and mobility of ions. Therefore, the zeolite deconstruction under hot liquid water can be described as a phenomenon that is more similar to the recrystallization that occurs under synthesis conditions than to a chemical attack, which explains the stability improvement obtained upon hydrophobization. Finally, the activity losses of the different zeolites in the presence of water have been evaluated by using the alkylation of m-cresol in a liquid biphasic system as a probe reaction, which is relevant to biomass conversion processes.

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1. Introduction

Upgrading of biomass-derived bio-oil to biofuels will face significant challenges since bio-oil is not particularly suitable for thermal fractionation or re-vaporization after it has been condensed from pyrolysis vapors. Therefore, conducting reactions at moderate temperatures in the liquid phase appears as an attractive approach. We have recently proposed to conduct catalytic conversion in liquid phase over pre-fractionated segments of bio-oil [1]. After condensation, the full bio-oil cannot be fractionated by conventional distillation since reheating this unstable liquid results in undesirable oligomerization reactions. However, there are different ways of accomplishing fractionation of the bio-oil during condensation, without the need to reheat it. One of them is to perform the thermochemical conversion in stages. For example, one can conduct sequential heating treatments at increasing temperatures [2–6], which can thermally break down biomass components (hemicellulose, cellulose, lignin) at incremental temperatures due to their increased thermochemical stability. Initial heating at temperatures

below 300 °C (first torrefaction) results in evolution of small oxygenates (primarily acetic acid and acetol) and water decomposed mostly from hemicellulose. Subsequent heating to 400 °C leads to breaking down of fractions richer in cellulose, producing mainly levoglucosan and hydroxymethyl furfural (HMF) [6]. In the final, fast-pyrolysis step (~550 °C), the more stable, lignin-rich fractions are decomposed, forming mostly phenolic compounds. We have proposed that after a multi-stage pyrolysis of lignocellulosic biomass at different temperatures and reaction time, the liquid product can be separated into light, medium, and heavy oxygenated components. Therefore, the product mixtures from different stages can be selectively upgraded in liquid phase via different reaction approaches. Alternatively, the fractionation of bio-oil can be done during the condensation of the vapors [7].

Either of the two options enhances the upgrading process greatly since it reduces the complexity of the problem of dealing with a variety of different chemistries simultaneously by replacing it with a series of simpler problems, dealt with in tandem. While the hydrotreating approach treats the entire bio-oil as a common system, in this case, with a preceding fractionation, one can attack different fractions differently. Specifically, from different bio-oil fractions one could (i) partially remove unstable oxygen functional

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groups, (ii) couple C–C bonds to elongate the carbon chain, and (iii) completely remove the remaining oxygen functionality. The light oxygenates, consisting of water-soluble compounds such as acetic acid, acetol, and acetaldehyde can undergo condensation reactions to reduce acidity and partially remove oxygen. For example, ketonization of acetic acid (or even acetol) produces acetone, an attractive building block that can be further coupled with sugar-derived compounds, such as furfurals [8]. Ketones can also be hydrogenated to alcohols, which in turn can be used as alkylating agents of phenolic compounds, via acid-catalyzed alkylation [9]. These products, with enlarged C-chain length, can undergo hydrodeoxygenation to produce long-chain hydrocarbons, with minimum loss in liquid yield. The sugar-derived compounds can either couple with acetone as mentioned above or undergo oxidation to produce acids, which can also be ketonized and further upgraded as discussed above. The phenolics from lignin fraction of biomass (heavy products) can be alkylated with light alcohols or can undergo direct hydrodeoxygenation.

Due to the high concentration of water-soluble compounds present in bio-oil and the low water solubility of the aimed products, biphasic emulsions stabilized by catalytic particles are a promising system that maximizes the interfacial exchange area for simultaneous reaction and separation [10–12]. Zeolites are active and selective catalysts for many reactions of interest in bio-oil upgrading in the vapor phase. However, in the presence of condensed water above 150 °C, the crystalline framework of zeolites tends to collapse [13–15]. A potential solution to improve the tolerance to hot liquid water is to reduce the hydrophilicity of the zeolite. Moreover, hydrophobic zeolites tend to preferentially locate at the water/oil interface, which not only helps stabilizing the emulsion but also enhancing the mass transfer of reactants and products. However, in general, hydrophobization of zeolites results in the loss of Brønsted acid sites, which are essential for reactions of interest, such as dehydration, alkylation, and oligomerization. An alternative method to increase hydrophobicity without reducing the density of acid sites is silylation (also known as silanation) of the external surface. Silane reagents containing hydrolyzable groups (chloro-, alkoxy-, etc.) have been extensively used to hydrophobize the surface of inorganic materials in diverse applications, including chromatographic columns, biomedical implants, nanoscale devices, glasses, adsorbents, and catalysts [16–18]. In the particular case of zeolites, silylation has been used to enhance the adsorption of organic molecules in water remediation [19,20] and photocatalytic reactions [21]. Similarly, silylated zeolites have been employed in gas separation membranes and shown improved permeability of CO₂ [22]. More closely related to our interests, silylated SBA-15 have been recently used in the selective dehydration of fructose to HMF catalyzed by sulfonic groups in the silanes [23].

In a recent study [14], we have shown that the characteristically low thermal stability of H-USY zeolites in hot liquid water can be greatly improved by functionalizing the external surface with octadecyltrichlorosilane (OTS). We pointed out that this approach could have a significant impact for the application of H-USY zeolites in the conversion of biomass in aqueous systems. We observed that hydrophobization with organosilanes makes the zeolites able to stabilize water/oil emulsions and catalyze alcohol dehydration and alkylation of *m*-cresol with isopropanol in the liquid phase, at high temperatures. We found that while the crystalline structure of an untreated H-USY zeolite collapses in a few hours when put in contact with a liquid medium at 200 °C, the functionalized hydrophobic zeolites kept their structure practically unaltered [14].

In this contribution, we describe a systematic study of H-USY zeolites functionalized with alkylsilanes of varying alkyl chain length (C2–C18). Three silylating agents were studied:

octadecyltrichlorosilane (OTS), hexyltrichlorosilane (HTS), and ethyltrichlorosilane (ETS). For the latter, two different loadings were employed: 0.5 mmole/g zeolite ETS0.5 and 1.5 mmole/g zeolite ETS1.5. We have investigated the structural tolerance of the various samples to liquid reaction media (in biphasic emulsion) as well as increasing partial pressures of pure water vapor until a liquid phase is formed, both at 200 °C. The losses in crystallinity, surface area, and microporosity were quantified by using physical characterization techniques (N₂ physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), infrared spectroscopy (DRIFTS)) as well as by using the alkylation of *m*-cresol in a liquid biphasic system as an indicator of the retention of catalytic activity.

Alkylation of phenolic compounds with small oxygenates in the liquid phase may become a key process in bio-oil upgrading. As recently proposed [1,24], alkylation of phenolics by small alcohols derived from the small oxygenates (acids, aldehydes) present in the water-soluble fraction of bio-oil is very efficient to retain this carbon in the liquid fuel range. Clearly, it is important to carry out C–C bond formation reactions (aldol, ketonization, alkylation) before carrying out the hydrodeoxygenation. Otherwise, the C2–C4 oxygenates become light gases. Alkylation of phenolics can be readily accomplished if small acids and aldehydes are first converted to ketones and these ones to alcohols. Conducting alkylation in biphasic (emulsion) reaction systems is highly advantageous. Phenolics and alkylate products are mostly soluble in organic phase; small alcohols are soluble in water. As we have reported previously [8,10], small hydrophobized particles not only can stabilize water/oil emulsions, but also can catalyze reactions at the interface of the biphasic mixture, minimizing the mass transfer limitations. In the case of zeolites, hydrophobization has the added advantage of improving the thermal stability, preventing the structural collapse that typically occurs when zeolites are immersed in hot liquid water, which is the focus of the present study.

2. Experimental

2.1. Sample preparation

The parent zeolite used in this study was a faujasite H-USY zeolite (Si/Al ratio: 30) supplied by Zeolyst International, product name CBV760. ICP analysis of the as-received zeolite was performed at Galbraith Laboratories. The measured Si/Al ratio on this sample was 29.7. It has been reported that to reach this high Si/Al ratio, the initial Y zeolite is steamed (twice) and acid leached, which may be responsible for the observed mesoporosity present even in the sample we call “untreated” (see Table 2). The silylation of the zeolite’s surface was performed by the same procedure as that described in our previous work [14]. That is, 1 g. of the parent H-USY zeolite was dispersed in 20 cc. of toluene with a horn-sonicator (Fisher Scientific 600 W, 20 kHz) operating at 25% amplitude for 1 h. The zeolite suspension was then added to a 50 cc. of organic solution containing the specific silane reagent OTS (purity 90%), HTS (purity 97%), or ETS (purity 98%) at a silane/zeolite ratio of 0.5 mmol/g zeolite. In addition, a second ETS sample was prepared using an organic solution with a higher silane/zeolite ratio, that is, 1.5 mmol silane/g zeolite. In each case, the resulting suspension was stirred for 24 h at 500 rpm at 30 °C in an IKA RCT B S1 lab hot plate/magnetic stirrer equipped with an ETS-D5 electronic contact thermometer. The zeolite was then filtered and washed thoroughly on a nylon filter (0.22 μm pore size) several times with ethanol and finally dried at 100 °C overnight. All the silane reagents, as well as *m*-cresol and isopropanol were purchased from Sigma-Aldrich and used as received.

Table 1
Carbon content in the silane-functionalized H-USY zeolites (Si/Al = 30) determined from thermogravimetric analysis (TG-DTA) and temperature-programmed oxidation (TPO) together with contact angle of a water droplet deposited over pelletized zeolite.

Silane-functionalized H-USY zeolite	Carbon weight %	μ moles of silane /g zeolite	Contact angle with water droplet (°)
OTS	5.7	265	135
HTS	2.4	330	126
ETS (1.5)	1.6	670	130
ETS (0.5)	0.8	315	9
USY	0	0	0

2.2. Characterization of the functionalized zeolites

The elemental analysis of the OTS-functionalized zeolite conducted by ICP at Galbraith Laboratories indicated that after the incorporation of the silanes, the measured Si/Al ratio was 33. A Perkin–Elmer Spectrum 100 FTIR equipped with a high-temperature DRIFT cell (HVC, Harrick) with CaF_2 windows was used to obtain diffuse reflectance infrared Fourier transformation spectra (DRIFT) of the functionalized zeolites before exposure to the liquid-phase reaction conditions. All the measurements were performed after heating 100 mg of the sample in situ up to 230 °C under a flow of He (30 ml/min) with a ramp of 10 °C/min and keeping them at this temperature for 30 min. A background spectrum was recorded in each run followed by 476 scans taken at a resolution of 4 cm^{-1} to get the final averaged spectrum.

Quantification of carbon loading in the functionalized zeolites was done by thermogravimetric analysis (TG-DTA) and temperature-programmed oxidation (TPO) using a Netzsch STA 449 F1 Jupiter TG-DTA. The sample (~20 mg) was placed in a cell and treated in air at 100 °C for 30 min, followed by a heating ramp of 10 °C/min to 800 °C, and a cooling ramp of 20 °C/min to 400 °C. Measurement of the variation of weight as a function of temperature was complemented with IR analysis of the evolved gases using a coupled Bruker Tensor 27 FTIR.

N_2 physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM) were used to characterize the functionalized and untreated H-USY zeolites before and after liquid-phase reaction. The N_2 adsorption isotherms were measured using a Micromeritics ASAP 2010 unit. Prior to analysis, the materials were degassed in situ for 22 h at 230 °C. The surface area was calculated from the BET equation in the 0.05–0.3 relative pressure range. The micropore volume and micropore area were obtained from the t -plot data (relative pressure range: 0.2–0.6). XRD patterns were collected on a D8 Series II X-ray diffractometer (BRUKER AXS), in reflection geometry using $\text{CuK}\alpha$ radiation generated at 40 kV and 35 mA in the 2θ range from 5° to 40°. Morphology of the samples was examined using scanning electron microscopy (SEM) on a FIB Zeiss NEON 40 High Resolution Scanning Electron Microscope operated at 5 kV. All samples were coated with 2-nm-thick Iridium providing excellent grain-free coating for high-resolution field emission (FE)-SEM imaging. The TEM samples for hydrophilic and hydrophobic crystals were prepared by applying a few droplets of aqueous and isopropyl alcohol suspensions of the particles, respectively, onto a copper grid coated with carbon. The grid was then allowed to air-dry. Transmission electron microscopy (TEM) investigation was conducted on a JEOL JEM-2100 Scanning Transmission Electron Microscope operating at 200 kV. All TEM images were recorded using a CCD camera.

2.3. Catalytic reaction measurements

Catalytic tests for alkylation of *m*-cresol with isopropanol over the various zeolite samples were carried out in a 300 ml Parr 4843 batch reactor. The temperature and pressure inside the

reactor were monitored with a CAL 9500P controller (CAL Controls Ltd.) and an Aschcroft transducer, respectively. In each reaction test run, a 0.5 g catalyst sample was dispersed in a 60 ml mixture of equal volumes of deionized water and decalin, sonicating for 15 min at 25% of amplitude. The mixture was placed in the stainless steel reaction vessel and purged with a 200 ml/min flow of He. Pressure was increased to 300 psig, while stirring at 240 rpm, and the reactor was heated up to 200 °C. At this point, 25 ml of a mixture of equal volumes of deionized water and decalin containing the reactants was injected from a pressurized feeding cylinder. Pressure of the reactor was adjusted to 700 psig with additional He, and finally, the gas inlet was closed to let the reaction proceed in the batch mode. At the end of the reaction period, the reactor was cooled to room temperature and depressurized. The zeolite was separated from the reaction mixture by centrifugation at 5000 rpm for 5 min. The aqueous and organic phases obtained after decantation of the zeolite were analyzed by gas chromatography (GC–FID and GCMS). An Agilent GC–FID 6890A equipped with a capillary column of polyethylene glycol (HP-INNOWAX) of 60.0 m $\times$ 0.32 mm $\times$ 0.25 μm nominal was used for quantitative analysis, while a Shimadzu QP2010S GC–MS equipped with an HP-INNOWAX polyethylene glycol capillary column, 30.0 m long $\times$ 0.25 μm nominal, was used for product identification. In all the GC–FID analyses, ethanol and 1,2-dichloromethane were used as internal standards to help close the mass balances. To minimize column damage, the aqueous fractions were extracted in methanol before injection.

Finally, to investigate the differences in crystallinity losses when the zeolites are exposed to gaseous or liquid water, we conducted a series of experiments at varying water partial pressures. In each experiment, the dry zeolite was placed in an autoclave and exposed to different amounts of water at 200 °C, resulting in varying conditions that went from overheated dry steam, to saturated vapor, to liquid water. After different exposure times, the resulting crystallinity of the various zeolites was characterized by XRD.

3. Results and discussion

The results of this study are presented and analyzed in four sections. The first deals with the physical characterization of the fresh zeolites after silylation, using silane reagents of different alkyl chain length. In this section, we analyze the hydrophobization imparted on the zeolite by the silylation procedure using different silane reagents. We have used DRIFTS to investigate the disappearance of OH groups upon silylation (that is, external silanols vs. internal acid sites). The second section describes the results of characterization techniques (N_2 physisorption, XRD, SEM, HRTEM, XPS) that we have used to evaluate the structural changes occurring on the various silylated samples before and after exposure to the hot liquid reaction system (water/oil emulsion). The third section compares the catalytic activity and selectivity changes that occur under *m*-cresol/isopropanol alkylation reaction conditions. Significant differences are observed among the various silylated samples resulting from using different silane reagents

(OTS, HTS, and ETS). In the last section, we investigate the effects of exposing the different zeolites to water vapor instead of the biphasic liquid reaction mixture. By varying the amount of water placed in contact with the dry zeolite, we have been able to control whether the zeolite was only exposed to water vapor or also to liquid. The extent of collapse of the crystalline phase seems to be directly related to exposure to water in the liquid phase.

3.1. Hydrophobization of H-USY zeolite by silylation

As demonstrated in Fig. 1 (left), the OTS, HTS, and ETS1.5-functionalized zeolites are highly hydrophobic and they are not wetted by water, but rather they become suspended in the decalin phase. When they are placed only in water, they remain on the surface of water, even after vigorous stirring. By contrast, the untreated H-USY zeolite and the ETS0.5 samples are essentially hydrophilic and get fully immersed in water. Furthermore, to study the wettability of the various silylated zeolites, a water droplet was placed from a pipette over pressed zeolite pellets. Two contrasting behaviors were observed. On the untreated H-USY zeolite, the water droplet fully wetted the surface (contact angle = 0) and was quickly absorbed in the pellet. On the OTS, HTS, and ETS1.5-functionalized zeolites, the droplet remained on the surface, keeping a high contact angle indefinitely, see angles in Table 1. Similar behavior has been reported for SBA-15 functionalized with C1–C8 silanes [25]. The ETS0.5, with a lower degree of functionalization, is still hydrophilic (contact angle = 9°).

It is interesting to note that while the samples functionalized with OTS and HTS exhibit similar hydrophobicity, the sample functionalized with the same molar silane concentration but with much shorter alkyl chains (ETS0.5) remains essentially hydrophilic. On the other hand, when the concentration of the ETS reagent was tripled, the resulting silylated zeolite exhibited hydrophobicity similar to those functionalized with OTS and HTS.

Fig. 2a shows the DRIFT spectra for the OH vibrational region (3500–3750 cm^{-1}) of the silylated samples compared to that of the untreated H-USY zeolite. The most prominent change observed upon silylation is the large decrease in intensity of the band centered at 3745 cm^{-1} . It is widely accepted that this band is associated with silanol groups located on the external surface of zeolites [26] and other silica-based materials [27,28]. This decrease in intensity is consistent with the widely proposed silylation mechanism, by which a surface OH group reacts with one of the chloro ligands in the alkyltrichlorosilane, resulting in alkylsilane groups covalently attached to the zeolite's surface.

An interesting result is the appearance of a band in the 3700–3710 cm^{-1} region on the samples functionalized with OTS, HTS, and (to a lesser degree) ETS1.5. By contrast, this band is not present

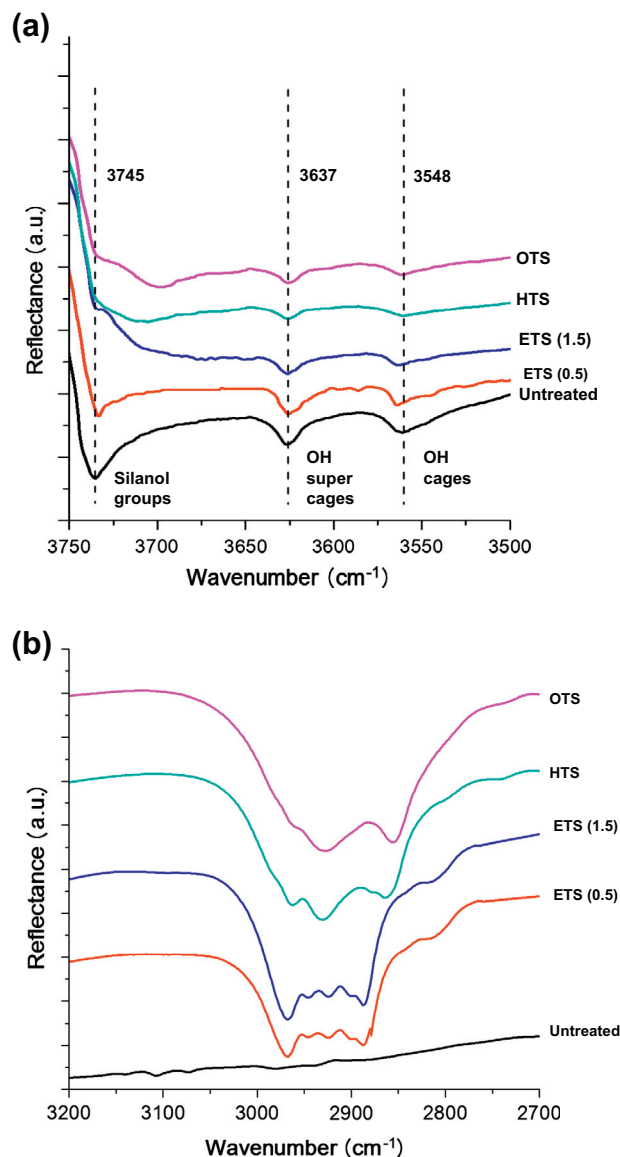


Fig. 2. DRIFT spectra of silane-functionalized H-USY zeolites compared to the untreated H-USY zeolite. (a) OH stretching region (b) C–H stretching region.

for the ETS0.5 sample. This new band appearing on the functionalized samples is due to a shift of the band corresponding to the residual external silanol groups interacting via H-bonding with

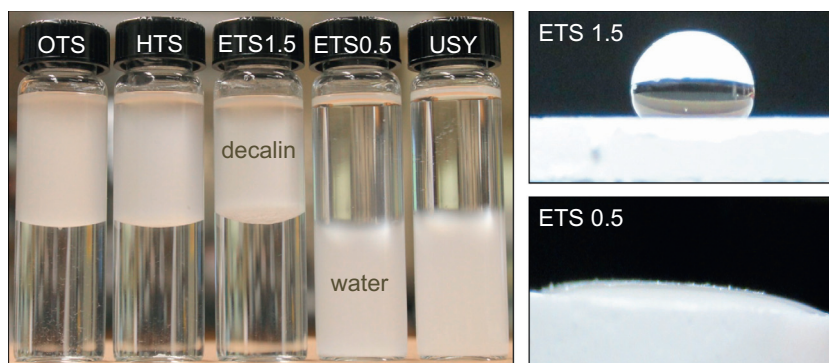


Fig. 1. Left: decalin/water suspensions of hydrophobic and hydrophilic zeolites. Right: water droplets in contact with pressed pellets of silane-functionalized H-USY zeolites (Si/Al ratio = 30). OTS: octadecyltrichlorosilane; HTS: hexyltrichlorosilane; ETS0.5 and ETS1.5: ethyltrichlorosilane.

the alkyl groups; the absence of this shift on the ETS0.5 sample is consistent with a lower degree of functionalization resulting on this sample.

As shown in Fig. 2a, the intensity of the bands associated with the high-frequency (HF) and low-frequency (LF) OH stretching modes (3637 and 3548 cm^{-1} , respectively [29,30]) were less affected by the functionalization than the silanols, which were greatly reduced. As previously discussed [14], this is a remarkable result since these bands are attributed to hydroxyl groups on the supercages and β -cages [31,32], respectively, which are responsible for the Brønsted acidity of the zeolite [31,33], which is required to catalyze the desired alkylation reaction [34]. In our previous study on hydrophobized zeolites [14], we demonstrated the resilience of the HY acid sites to the functionalization by adsorbing pyridine, which showed IR bands similar in intensity to those observed with the unfunctionalized USY zeolite.

Fig. 2b shows the DRIFT spectra for the C–H stretching region (2700 – 3200 cm^{-1} [35]) of the silylated samples. These bands are similar to those observed on alkylsilane-functionalized silicon oxides [36] and are not present for the untreated H-USY zeolite. As expected, the intensity and band distribution in this region vary for the different alkyl chains. In fact, the strongest bands observed for the ETS sample appear near 2965 and 2872 cm^{-1} , which are the expected frequencies for C–H stretching of methyl (CH_3) groups, which are dominant in these short chains. By contrast, the most intense bands for HTS and particularly OTS samples are near 2920 and 2853 cm^{-1} , corresponding to the C–H stretching of methylene (CH_2) groups, which dominate in the longer chains [37]. We conducted TG-DTA (with IR analysis of the gas phase) combined with temperature-programmed oxidation (TPO) to quantify the extent of zeolite functionalization with each silane agent. The TG-DTA results are shown in the Supporting information file. Overall, the weight loss patterns are similar for all samples. First, a small loss is observed during the isothermal 40-min period at 100°C . A more significant second loss is obtained between 200 and 300°C (max. $\sim 250^\circ\text{C}$), and more pronounced losses are seen in the range 350 – 600°C . IR spectra of the gas phase obtained during the temperature ramp mainly exhibit bands for CO_2 (2280 – 2390 cm^{-1}), CO (2100 cm^{-1}), hydrocarbons (2800 – 3000 cm^{-1}), and H_2O (numerous peaks centered at 1600 and 3790 cm^{-1}). As summarized in Table 1, the amount of carbon evolving from each functionalized zeolite follows the expected trends; i.e., more carbon from longer alkyl chains ($\text{OTS} > \text{HTS} > \text{ETS}$), and with increasing concentration during silylation ($\text{ETS1.5} > \text{ETS0.5}$). However, converting the C wt% to moles of silanes, it is clear that silylation with the longer alkyl chain (OTS) results in a lower density of silane groups on the surface than with the shorter chains (ETS and HTS). Also, when a higher concentration of short alkyl silane was used (ETS1.5), the density was the highest.

3.2. Structural changes on the various silylated zeolites after exposure to biphasic liquid reaction mixture at 200°C

N_2 adsorption isotherms were obtained for the silane-functionalized and untreated H-USY zeolites before and after 22-h reaction (see Fig. S1). All isotherms have the typical type IV shape indicating the presence of micro- and mesopores. The structural data derived from these adsorption data are summarized in Table 2. First, on the fresh samples, it can be noticed that functionalization of the H-USY zeolite surface causes a modest reduction in microporosity. Since the XRD shown below demonstrate that this loss in microporosity is not accompanied by a comparable loss in crystallinity, it is probably due to partial blockage of the zeolite pores by the functional groups, as recently suggested [38]. The trends observed on the fresh samples are consistent with the TGA/DTA and IR results. That is, the extent of pore blockage increased as the length of the alkyl

chain increased (i.e., $\text{OTS} > \text{HTS} > \text{ETS0.5}$). Also, the ETS-functionalized zeolites with different loadings showed increased pore blockage as the concentration of alkylsilane increased ($\text{ETS1.5} > \text{ETS0.5}$).

Second, the samples exposed to 22 h of reaction in a biphasic water/oil mixture at 200°C showed dramatic difference in surface area and microporosity losses depending on the type and amount of functional groups attached to the zeolite. That is, on the untreated H-USY zeolite, both the BET area and micro/mesopore area ratio decreased significantly after reaction, due to the collapse of the microporous crystalline structure of the zeolite and consequent formation of a mesoporous amorphous silica-aluminate. By contrast, the silane-functionalized zeolites exhibited a remarkable tolerance to the reaction medium with only small losses in BET area and microporous structure. The only functionalized sample that did not exhibit the same tolerance was the ETS0.5 zeolite, which had shown high hydrophilicity when suspended in water (see Fig. 1). However, when the extent of functionalization was increased (ETS1.5) and the zeolite became hydrophobic, the tolerance to the reaction medium increased greatly.

The XRD patterns of both untreated and silane-functionalized H-USY zeolites had similar degree of crystallinity before exposure to the biphasic liquid reaction mixture (see Fig. S2). Only a slight decrease in the overall intensity of the diffraction peaks due to modification of the zeolite surface [39] was observed on the functionalized samples. As expected, this effect is more pronounced for low diffraction angles (2θ). After 22-h reaction in the biphasic liquid mixture, the differences are dramatic. While the XRD pattern of the untreated H-USY showed a total loss in crystallinity, those functionalized with OTS, HTS, and ETS retained a large fraction of their crystalline structure. Fig. 3 shows the time progression of relative crystallinity calculated by integration of the areas under the diffraction peaks (see Table S1). While the difference between the untreated H-USY and the OTS, HTS, and ETS1.5 is obvious and in line with the differences shown above, it is interesting to analyze the time evolution observed for ETS0.5. During the first few hours, the crystallinity of this sample decreased at a rate comparable that of the untreated sample. However, after about 5 h, it started to collapse at a much lower rate, similar to that of the other functionalized samples.

A comparison of the functionalized samples with different alkyl lengths shows that the length of the functional group seems to have a positive effect on the stability of the zeolite in the biphasic medium. That is, while the OTS sample contains a lower density of functional groups per gram of zeolite than HTS, ETS0.5, or ETS1.5, it is much more stable under the biphasic liquid mixture. As will be shown below, this trend is not the same when the zeolites are exposed only to water. Therefore, it seems that in the biphasic system, the longer (more lipophilic) functional groups enhance the protection of the zeolite, perhaps attracting a layer of organic molecules near the external wall, which further protect the microstructure.

For the same type of group (i.e., ETS), the density of functionalization has an obvious effect. That is, ETS1.5 was much better than ETS0.5 in preventing the collapse of the zeolite structure.

To visualize the differences in structural stability of the functionalized samples, SEM images were obtained before and after reaction in the biphasic liquid mixture. As shown in Fig. 4, the collapse in crystalline structure demonstrated above by XRD and N_2 adsorption causes evident topology changes, easily observed by SEM. The characteristic crystals of the untreated H-USY zeolite, with a rather smooth external surface, are replaced by amorphous aggregates resembling precipitated materials. To investigate the progression of this transformation, we conducted SEM analysis on samples of the untreated H-USY zeolite as a function of exposure time to the biphasic liquid mixture. Fig. 5 shows the gradual transformation of the zeolite crystals as a function of time. After

Table 2

Specific area (S_{BET}), micropore volume (V_{micro}), and ratio mesopore/micropore area ($S_{\text{meso}}/S_{\text{micro}}$) of silane-functionalized H-USY zeolites compared to the untreated H-USY zeolite before and after reaction for 22 h at 200 °C and 700 psi in He. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M.

Sample	S_{BET} (m ² /g)	% Decrease S_{BET}	V_{micro} (cm ³ /g)	% Decrease V_{micro}	$S_{\text{meso}}/S_{\text{micro}}$
<i>OTS-functionalized HY</i>					
Before reaction	473.47		0.2		0.11
After reaction 22 h	377.64	20	0.12	40	0.58
<i>HTS-functionalized HY</i>					
Before reaction	572.22		0.26		0.13
After reaction 22 h	397.37	30	0.14	46	0.42
<i>ETS-functionalized HY (1.5 mmole/g)</i>					
Before reaction	550.42		0.26		0.11
After reaction 22 h	415.82	24	0.16	38	0.30
<i>ETS-functionalized HY (0.5 mmole/g)</i>					
Before reaction	630.25		0.29		0.11
After reaction 22 h	322.90	49	0.13	55	0.26
<i>Untreated HY</i>					
Before reaction	692.54		0.32		0.11
After reaction 22 h	116.07	83	0.02	94	2.28

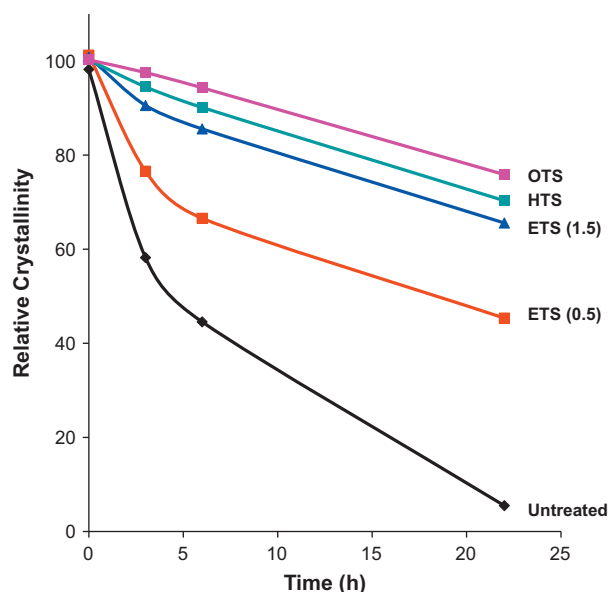


Fig. 3. Evolution of zeolite crystallinity (measured by integrating the areas under the X-ray diffraction peaks) as a function of reaction time at 200 °C and 700 psi in He in an emulsion system. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M.

0.5 h, nucleation spots start appearing on the external surface of the crystals, which still retain a significant part of their original shape. After 3 h, the nucleation sites seem to have grown into larger amorphous aluminosilicate aggregates. This progression gives some insight into the possible pathway of the process of zeolite collapse, which can be described as a metamorphosis of a crystalline (but open) structure into an amorphous (but denser) solid. The liquid medium provides a favorable environment for this transformation, which necessarily involves the dissolution of species from the zeolite structure and re-precipitation of this species, converting the metastable zeolitic crystal to a more stable amorphous aluminosilicate. It is well known that this metastability is due to the high surface enthalpy of zeolites that arises from their high internal surface area, which may make the crystalline structure of a zeolite thermodynamically less stable than an amorphous, but denser, aluminosilicate [40,41].

In Figs. 6–8, we compare the topology of the crystals before and after 22-h reaction for the OTS, ETS1.5, and ETS0.5-functionalized

zeolites. The SEM images show that, before reaction, the functionalized samples have practically the same characteristic crystals of the untreated H-USY zeolite, with an external surface as smooth as the pattern zeolite. As opposed to the drastic changes in topology observed on the untreated zeolite after 22-h reaction, the crystalline structure of the OTS- and ETS1.5-functionalized samples remains practically unchanged, in agreement with the XRD results. By contrast, the ETS0.5-functionalized zeolite (Fig. 8), while still keeping the overall shape of the original crystals, exhibits the presence of nucleated aggregates on the external surface of the crystals.

Fig. 9 shows HRTEM images of the untreated H-USY zeolite before and after reaction. The effects of the transformation after reaction are obvious. While the images of the fresh sample exhibit the typical microcrystalline structure, the spent sample is totally amorphous with clear evidence of increased mesoporosity. In this regard, it is important to point out that the untreated H-USY zeolite already has some mesoporosity, produced during the manufacture of the USY zeolite. It is well known that to reach the high Si/Al ratio of this zeolite (30), steaming and acid leaching has to be conducted by the manufacturers on the original Y zeolite (Si/Al ~ 2–3). This treatment produces some mesopores, as clearly seen in the HRTEM images (see arrow m). As discussed below, these mesopores play a critical part during the transformation in the presence of water vapor because condensation occurs in these pores at water partial pressures lower than the saturation pressure.

Figs. 10 and 11 illustrate, respectively, the characteristic HRTEM images of the ETS1.5- and ETS0.5-functionalized H-USY zeolites for the fresh samples (top) and after 22-h reaction at 200 °C and 700 psi (bottom). It is observed that while the ETS1.5 retains its crystallinity after reaction, the ETS0.5 sample shows regions that have become amorphous, while other regions retain their crystallinity, a result that agrees well with the partial decrease in crystallinity measured by XRD.

3.3. Structural changes of the silylated zeolites after exposure to water vapor at 200 °C

The above results have shown that the crystalline structure of the untreated H-USY zeolite collapses in the presence of biphasic liquid reaction mixture at 200 °C. It has been proposed that the attack of the crystalline structure is due to a chemical reaction between Si–O–Si bonds and a water molecule [13]. If this was the rate-limiting step for the zeolite reconstruction, the rate of collapse would be determined by the chemical potential of the water molecule inside the zeolite, which in turn is the same as that of the

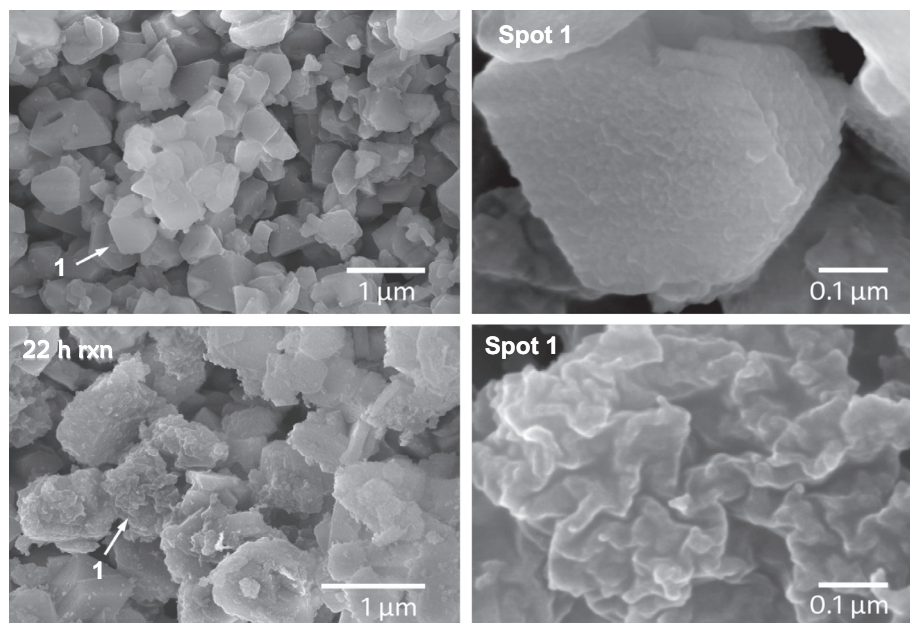


Fig. 4. SEM images of the untreated H-USY zeolite (Si/Al = 30); top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He in an emulsion system. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Left: Low magnification. Right: High magnification of region of the arrow.

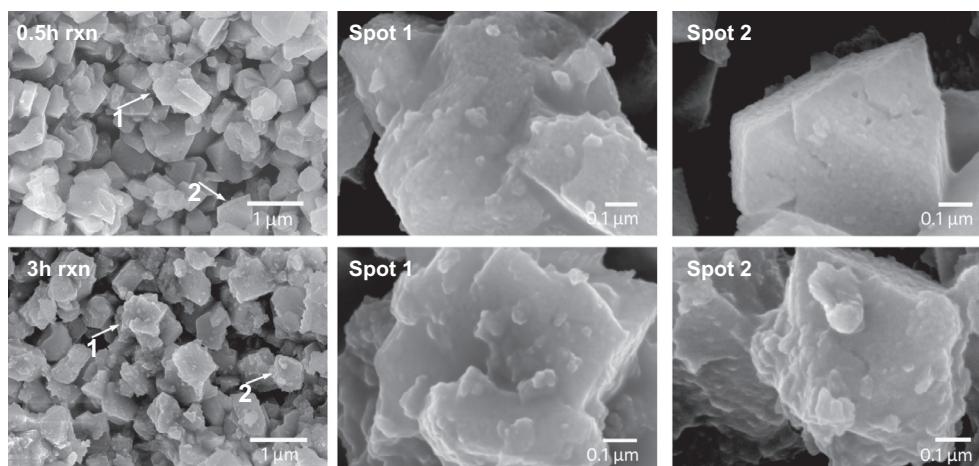


Fig. 5. SEM images of the untreated H-USY zeolite (Si/Al = 30) at different reaction times. Reaction conditions include: 200 °C and 700 psi of He in an emulsion system. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Top: 0.5 h; bottom: 3 h. Center and right: higher magnification of regions of the arrows.

water vapor outside the zeolite, given essentially by the partial pressure of water in the vapor phase, regardless of the presence or absence of a liquid phase. To test this hypothesis, we have conducted a series of experiments in the presence of steam as well as liquid water. As the amount of water in the system is high enough to reach saturation, the chemical potential will not increase with increased amounts. However, the amount of liquid water will. The results shown below demonstrate that the extent of crystalline losses is a function of the amount of condensed water present rather than the chemical potential of water.

Fig. 12 illustrates how the experiments were conducted. In each run, 0.5 g of dry zeolite was placed in an autoclave, suspended in a basket. Different amounts of water were placed at the bottom of the autoclave, not directly in contact with the zeolite. Then, the 60-ml autoclave was heated up to 200 °C to generate steam at the autogenic pressure. The vapor pressure of water at this temperature is 18.6 atm. Under these conditions, the gas compressibility factor for water is about 0.96. Therefore, 30 mmoles (n_0) of water

will be required to reach the saturation of the vapor at this temperature in the 60 ml volume. We use the n/n_0 ratio to represent the amount of liquid water placed in the autoclave for each experiment plus the amount of water already present inside the zeolite (determined to be 2.78 mmol for 0.5 g zeolite) relative to the number of moles at saturation (n_0). That is, one would not expect liquid water on a flat surface when $n/n_0 < 1$; however, capillary condensation may occur in the mesopores of the USY zeolite at significantly lower n/n_0 values.

Fig. 13 shows the XRD results after exposing the untreated H-USY zeolite to water 200 °C at $n/n_0 = 5$, that is, with condensed water present. A drastic loss in crystallinity is observed, which is much more pronounced than that observed during reaction at the same temperature in the biphasic system (see Fig. 3). This difference indicates that the presence of an organic phase has some protective effect against water, even with the hydrophilic zeolite. Of course, the stability of the zeolite in pure water gets much improved on the silane-functionalized samples. However, as shown in Fig. 14, the most

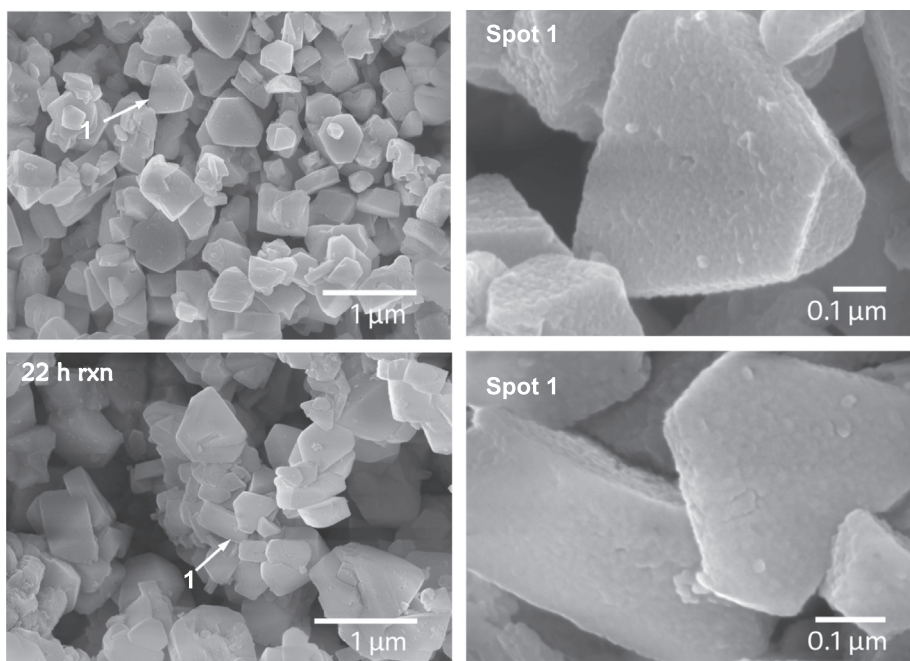


Fig. 6. SEM images of the OTS-functionalized H-USY zeolite; top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He in an emulsion system. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Left: low magnification. Right: high magnification of region of the arrow.

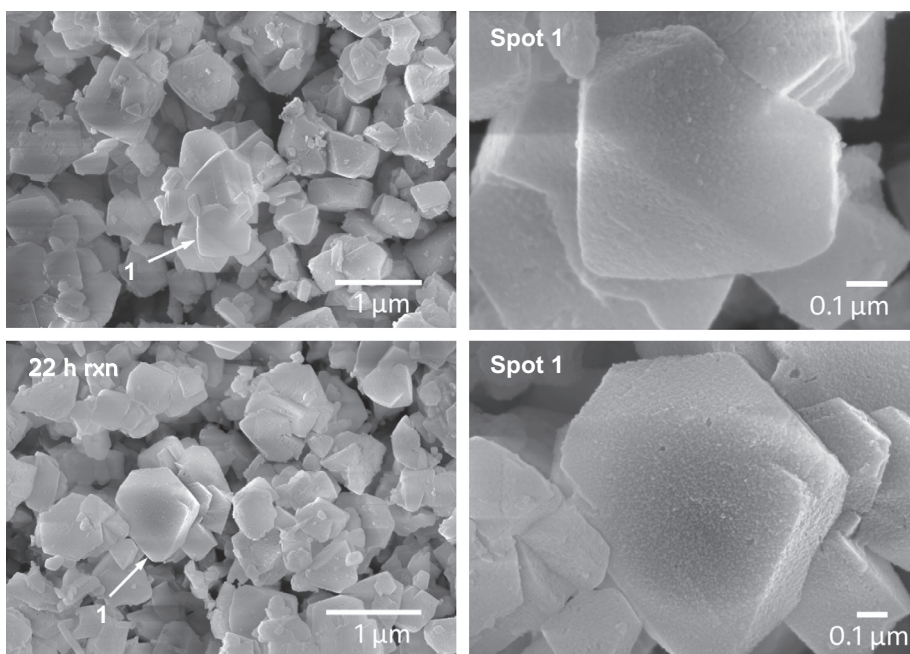


Fig. 7. SEM images of the ETS1.5-functionalized H-USY zeolite; top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Left: low magnification. Right: high magnification of region of the arrow.

stable sample is now the zeolite functionalized with ETS1.5. Interestingly, the zeolite functionalized with the longer alkyl chains (OTS), which showed the highest stability during reaction in the biphasic system, became less stable in pure water. As shown in Fig. 15, the stability trend is now ETS0.5 ~ HTS < OTS < ETS1.5.

Determining under what conditions there is liquid water present is not straightforward since it will depend on the distribution of mesoporosity in the sample. As shown in Fig. 16, when the partial pressure of water in the system is below that needed for water condensation the loss of crystallinity after a 6 h-treatment was

negligible, which is a clear indication that it is the presence of liquid water what determines the collapse in crystallinity. In fact, when the zeolite was treated at 200 °C under $n/n_0 = 0.4$ for 18 h, the crystallinity remained above 96%. When the amount of water in the system was $n/n_0 = 0.6$, just above the onset of condensation, the loss in crystallinity was not as high as when the amount of liquid water was significant, but still noticeable.

From the Kelvin equation, one can calculate what would be the mesopore diameter needed to begin having liquid water under these conditions. With a value of 0.042 N/m for the surface free

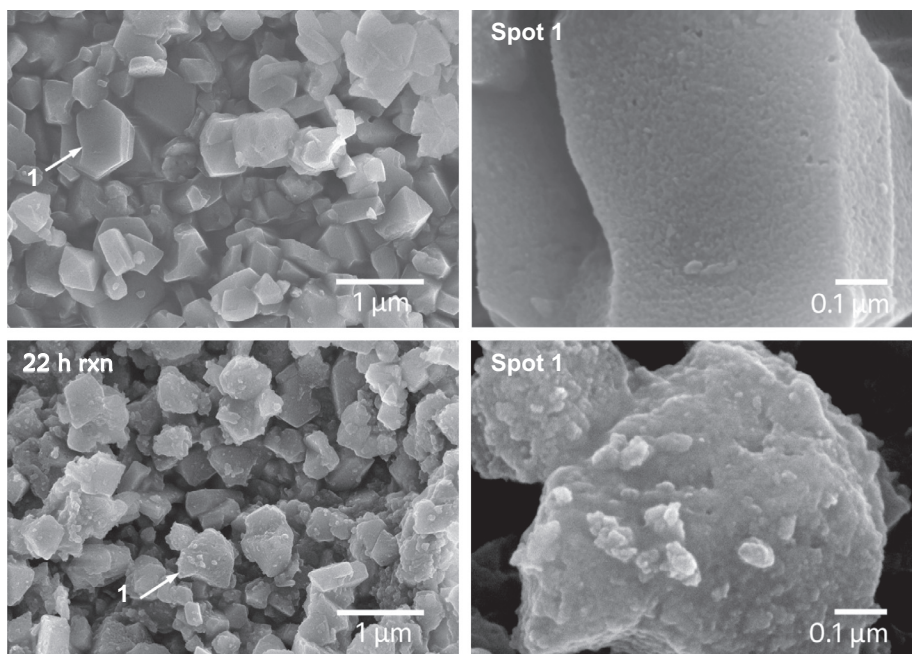


Fig. 8. SEM images of the ETS0.5-functionalized H-USY zeolite; top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Left: low magnification. Right: high magnification of region of the arrow.

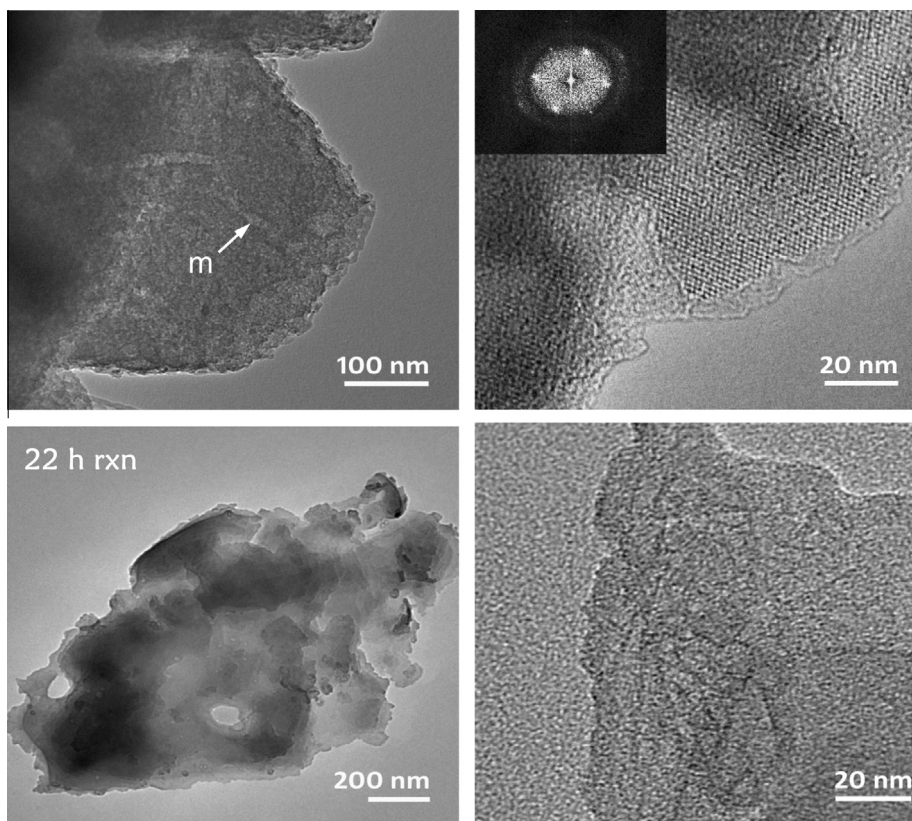


Fig. 9. HRTEM of the untreated H-USY zeolite (Si/Al = 30); top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Low magnification. Right: high magnification. Arrow m points to a mesopore.

energy of water at 200 °C and a molar volume of 18 cc/mol, the corresponding diameter for capillary condensation would be around 1.5 nm. One can envision that condensation might begin in very small defect pockets in the zeolite crystal, and these would be

the location of the initial water attack. Finally, when the amount of water exceeds $n/n_0 = 1$, even by a small amount, the extent of the attack is dramatic. As shown in Fig. 16, after 6 h, the zeolite is essentially amorphous (i.e., no diffraction peaks in XRD).

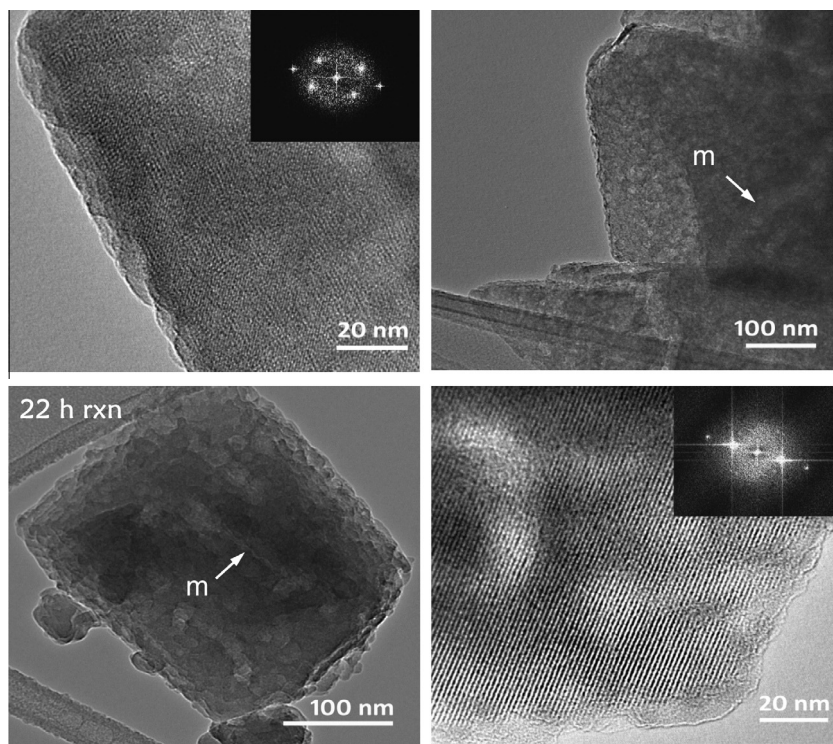


Fig. 10. HRTEM of the ETS1.5-functionalized H-USY zeolite; top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Low magnification. Right: High magnification. Arrow m points to a mesopore.

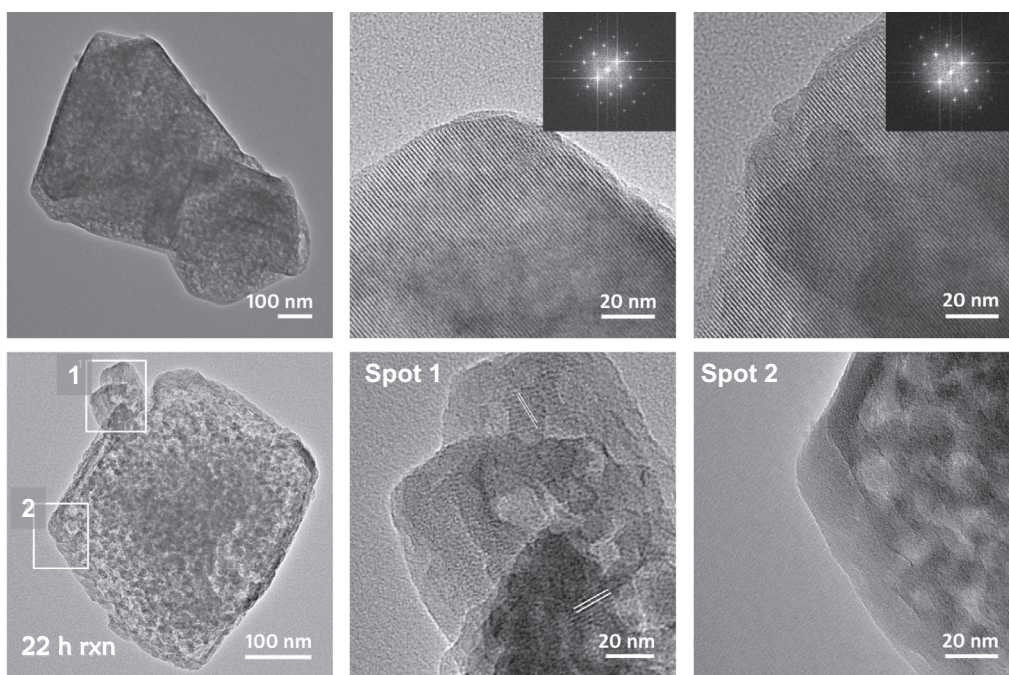


Fig. 11. HRTEM of the ETS0.5-functionalized H-USY zeolite; top: fresh; bottom: after 22-h reaction of m-cresol and isopropanol at 200 °C and 700 psi of He. Feed: isopropanol/m-cresol (3/1 M ratio); total molar concentration: 2 M. Low magnification. Right: high magnification.

It is important to compare the results observed here with those typically observed during dealumination of HY zeolites by steaming. At the conditions of the conventional hydrothermal (steaming) treatment of zeolites, only dry steam is present, i.e., the partial pressure of water is $\ll 1$ atm and the temperature > 550 °C [42,43]. Under these conditions, dealumination occurs via partial hydrolysis of Al–O bonds in the framework, producing octahedrally

coordinated non-framework Al species, which concentrate at or near the crystallite surface [44,45]. It has been experimentally established that the extent of dealumination increases proportionally to the partial pressure of steam [43]. This is the expected behavior for a gas–solid reaction in which the extent of reaction will be proportional to the chemical potential of the reactant (water). Being far from the point of saturation, the partial pressure

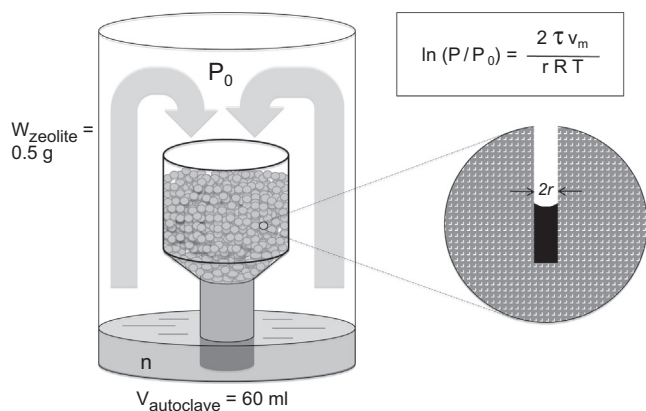


Fig. 12. Apparatus used to study the exposure of H-USY zeolite to water vapor at increasing partial pressures. The zeolite is suspended in a SS basket inside a 60-cc autoclave. Different amounts of water are placed at the bottom of the autoclave, not directly in contact with the zeolite. The autoclave is heated to 200 °C to generate steam at the autogenic pressure. Water condenses above 18.6 atm on flat surfaces or at the pressure (p) determined by the Kelvin equation on small pores or voids of radius r .

(and therefore the chemical potential) of water will obviously increase proportionally to the amount of water present in the system.

A very different situation occurs in our case; the chemical potential of water should not increase with the addition of water in excess of $n/n_0 = 1$. However, as shown in Fig. 17, the extent and rate at which the crystalline structure collapses is much higher for the case of $n/n_0 = 5$ than for the case of $n/n_0 = 1.1$. While the sample treated for 2 h at $n/n_0 = 1.1$ still retains about 50% of its original crystallinity, the one treated for the same time at $n/n_0 = 5$ has lost practically all its crystal structure. This is an important result, since

the chemical potential of water at any point of attack of the zeolite is the same in both cases, i.e., that in equilibrium with 21.8 atm of water vapor, what will vary with n/n_0 is the amount of liquid water present in the system. Therefore, it becomes clear that the condensed water in contact with the zeolite plays an important role in the process of zeolite deconstruction. The role of the organic functionalization is now clear, since it prevents the direct contact of the zeolite with condensed water phase. However, another very important effect of the silane functionalization is for the cases in which $n/n_0 < 1$. In these cases, the only places in which condensed water may be present is in the small pockets inside the zeolite (defective places). When the silane molecule is small enough, hydrophobization by silylation will also occur on the silanol groups present on the defects and mesoporous inside the zeolite structure. These sites would be the first to be wetted by liquid water and therefore the sites of water attack.

It is therefore demonstrated that the zeolite collapse is associated with the presence of a liquid phase at high temperature, which are conditions in which dissolution of crystals and mobility of ions becomes important. In fact, in this sense, we can think of the zeolite deconstruction by hot liquid water as a phenomenon very similar to the well-known zeolite recrystallization occurring under synthesis conditions [46]. For example, metastable faujasite transforms to other crystal structures such as ZSM-4 or P zeolite depending on the chemical environment and presence of nucleation sites [47]. Similarly, when fully crystallized A zeolite is left for longer times in its mother liquor, it recrystallizes to P zeolite [48]. While in these cases, additional Si was needed to favor the transformation to a structure of a higher Si/Al ratio, there are examples of transformations that occur without the presence of extra nutrients. One of them is the solution-mediated transformation of zeolite A into sodalite [49,50], which takes place under high OH concentrations, without added Si, since the two structures have the same Si/Al ratio.

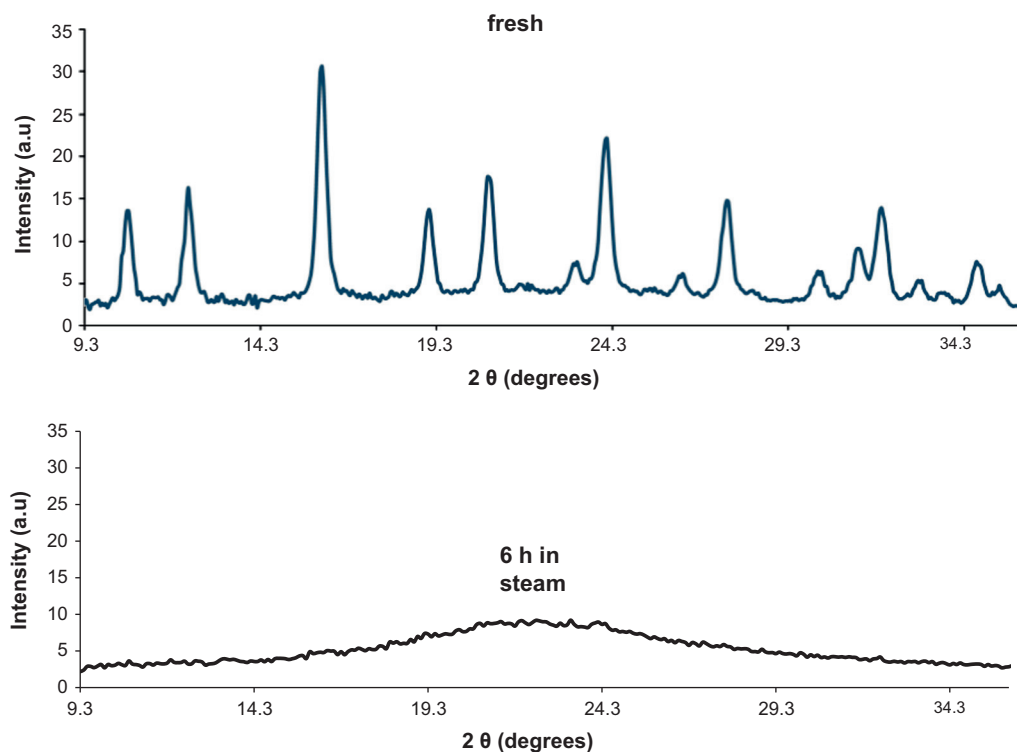


Fig. 13. X-ray diffraction patterns of the untreated H-USY zeolite before (top) and after (bottom) 6-h exposure at 200 °C to an amount of water added to the autoclave $n/n_0 = 5$, relative to that required to start condensation on a flat surface (n_0).

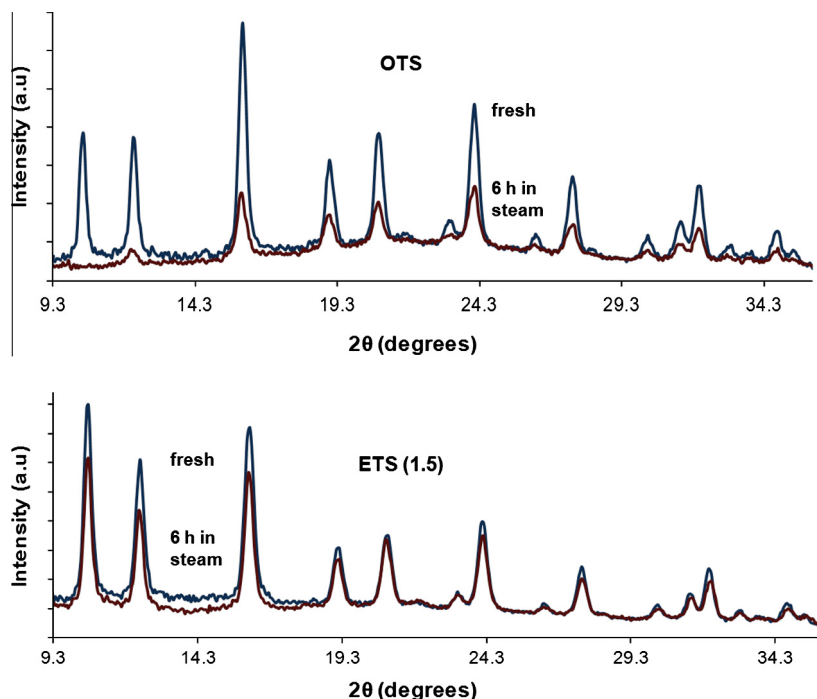


Fig. 14. X-ray diffraction patterns of the OTS – (top) and ETS1.5-functionalized H-USY zeolite (bottom) before and after 6-h exposure at 200 °C to an amount of water added to the autoclave $n/n_0 = 5$, relative to that required to start condensation on a flat surface (n_0).

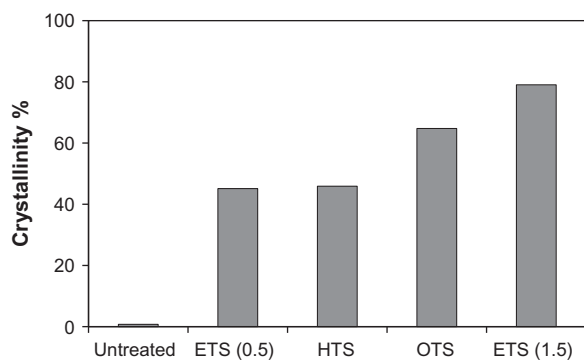


Fig. 15. Percent crystallinity retained in the different silane-functionalized H-USY zeolites after 6-h exposure at 200 °C as a function to the amount of water added to the autoclave relative to that required to start condensation on a flat surface (n_0).

An important question that could be asked at this point is the following. If liquid water attack occurs in cavities and defects about 1.5 nm in diameter, why does not the attack happen in the supercages of ~ 1.3 nm in size in which water may also condense? The difference is that, in this case, the liquid water is interacting with the walls of a perfect crystal. Therefore, one can conclude that two aspects are simultaneously required for the zeolite collapse by water attack. The first one is the presence of liquid water that facilitate solvation and mobility of ions. The second one is the presence of defects that make the chemical attack possible. Neither condition alone is enough to cause the collapse of the crystalline structure. If there are no defects present, the reactivity of the wall would be too low to react, even in the presence of liquid water. If water is not present in the liquid form, the attack would not proceed either, even in the presence of defective sites and under the same chemical potential of water (i.e., that of 16.8 atm vapor) due to the lack of solvation and ion mobility. Therefore, the role of hydrophobization via silylation may be twofold. Not only it prevents the direct interaction of the solid with liquid water but also it may also titrate defect sites (silanols), making the attack less likely.

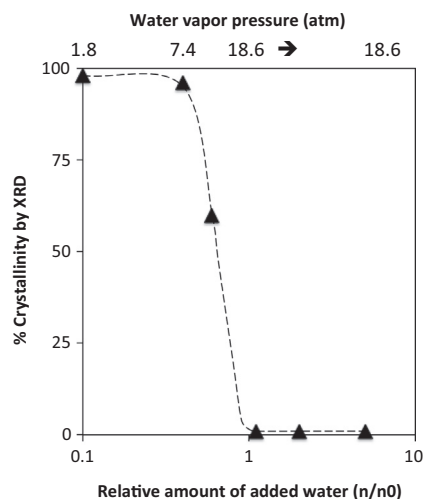


Fig. 16. Percent crystallinity retained in an untreated H-USY zeolite after 6-h exposure at 200 °C as a function to the amount of water added to the autoclave relative to that required to start condensation on a flat surface (n_0).

Fig. 18 compares water uptakes measured at room temperature on the untreated and OTS-functionalized zeolites. The partial pressure of water in this experiment was much lower than the vapor pressure of water at this temperature. Therefore, the uptake is only due to adsorption and no condensation can be expected in this case. Remarkably, when the uptakes are normalized to the BET areas measured by N_2 adsorption, the water adsorption evolution curves are within the experimental error. That is, in the absence of water condensation, the water uptake is not a function of the hydrophilicity or hydrophobicity of the zeolite. Since the water coverage on the internal sites of the zeolite is equilibrated with the chemical potential of the water molecules in the gas phase, outside the zeolite, the identical uptakes (normalized to the total BET) indicate that the functionalization does not affect the nature of the sites inside the zeolite. At the same time, these results

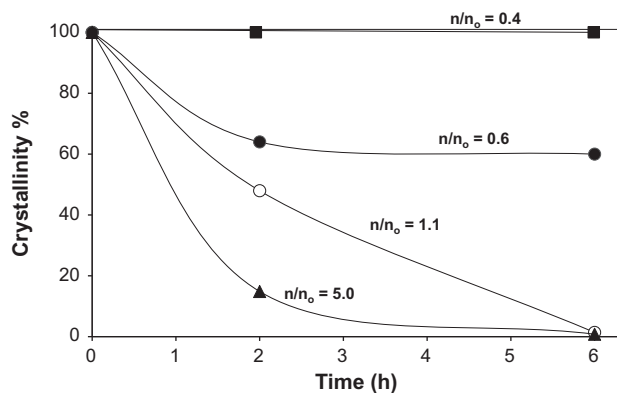


Fig. 17. Percent crystallinity retained in an untreated H-USY zeolite as a function of time of exposure at 200 °C to different amounts of water added to the autoclave relative to n_0 .

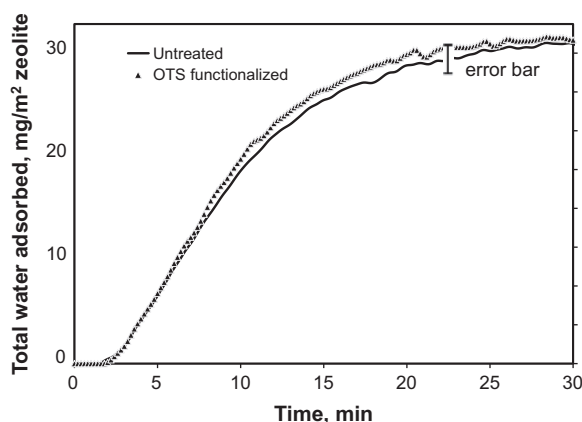


Fig. 18. Thermogravimetric analysis of the water adsorption per surface area (as determined by BET) over untreated and OTS-functionalized zeolites at 50 °C under a flow of 10 ml/min Argon saturated with water. All the samples were pretreated at 230 °C for 2 h with a 10 ml/min of dried Argon.

indicate that hydrophobization does not prevent the diffusion of water, and thus, as shown below, when water is present outside the zeolite, it will compete for adsorption sites on the hydrophobic zeolite as much as on the hydrophilic one.

3.4. Catalytic activity of the silylated zeolites in biphasic liquid reaction mixture

We have recently shown [14] that hydrophobized H-USY zeolites are effective as emulsion stabilizers as well as catalysts for Brønsted acid-catalyzed reactions in biphasic systems, e.g., dehydration and alkylation. In this case, we have used the alkylation of *m*-cresol with isopropanol as a probe reaction to compare the various silanes. Table 3 summarizes the different extents of *m*-cresol conversion obtained over the untreated and functionalized zeolites at 200 °C after 3 and 22 h in a batch reactor operating in emulsion.

The activity trend for the various zeolites follows very closely the observed stability trends. As expected, the untreated zeolite, which was the sample that most rapidly lost its crystallinity, is the one with the lowest activity at the end of the 22-h reaction period. Interestingly, even after the shorter reaction period (3 h), the untreated zeolite had a much lower activity than the silane-functionalized zeolites. Only the ETS0.5 sample had a lower activity than the untreated zeolite after 3 h. This is in agreement with

the fast drop in crystallinity shown for this sample during the first few hours in the reaction mixture (see Fig. 3) combined with the decreased surface area and microporosity resulting from the initial functionalization. By contrast, on the samples with longer alkyl groups (HTS, OTS) or with higher functionality density (ETS1.5), the initial losses in surface area and microporosity were overcompensated by the higher stability of the zeolite structure. The OTS-functionalized zeolite kept its activity reaching almost 100% conversion after 22-h reaction.

The ratios of di- to mono-alkylated products are also included in Table 3. Regardless of the type of silane group used, the multiple-to mono-alkylate ratio seems to increase with *m*-cresol conversion. This increase indicates that mono-alkylates are primary products that are subsequently further alkylated to di-alkylates and even tri-alkylates, to a much lower extent.

The evolution of catalyst activity, rate of deactivation, and distribution of products as a function of reaction time was investigated in a batch reactor operating in both, single organic phase and biphasic water/oil emulsions. To obtain each point at a given reaction time, a separate reaction run was conducted with *m*-cresol and isopropanol at 200 °C and 700 psi of He for four different cases:

- untreated H-USY in decalin single phase,
- OTS-functionalized H-USY in decalin single phase,
- untreated H-USY in water/decalin emulsion,
- OTS-functionalized H-USY in water/decalin emulsion.

When the reaction was conducted in decalin solvent, in the absence of water, the reaction rate was relatively high, reaching about 80% conversion in 8 h on both, the untreated and OTS-functionalized H-USY zeolites. In the presence of water, the initial activity was lower than in the absence of water for both catalysts, showing that water competes with active sites on both, untreated and OTS-functionalized H-USY zeolites. However, the most important difference, in agreement with the discussion presented above, was the drastic rate of deactivation presented by the untreated zeolite, which became practically inactive after about 2 h in the reaction medium.

To better quantify these differences, we have conducted a simplified kinetics analysis based on the following reaction pathway (see Table 4):

- Dehydration of isopropanol to propylene.
- Propylene alkylation of *m*-cresol to mono-alkylated cresol isomers.
- Secondary alkylation of mono-alkylated to di-alkylated-cresol isomers.
- Tertiary alkylation of di-alkylated to tri-alkylated-cresol isomers.
- Polymerization of *m*-cresol and alkylated-cresols.

The individual fittings of the concentrations of each species as a function of reaction time are shown in the Supporting information file. Fig. 19 illustrates the goodness of the overall fitting for all 4 cases. As seen in Table 5, in the decalin solvent, the OTS-functionalized zeolite has an intrinsic activity about 30–40% lower than the untreated zeolite for both dehydration and alkylation steps, in good agreement with the observed BET surface area, which as mentioned above can be rationalized in terms of pore blockage [14].

Moreover, interesting trends are observed when water is present in the system. First, both, the untreated and OTS-functionalized catalysts show a similar drop in activity compared to the reaction in the absence of water. This result is in agreement with the water uptake measurements shown above and indicates that in both

Table 3

Conversion of m-cresol and di-/mono-alkylated products ratio from the alkylation reaction of m-cresol and 2-propanol at 200 °C and 700 psi of He over untreated and functionalized HY zeolite (Si/Al molar ratio: 30). Feed: isopropanol/m-cresol molar ratio: 3; total molar concentration: 2 M.

Zeolite	3 h rxn		22 h rxn	
	m-Cresol conversion	Di/mono-alkylated ratio	m-Cresol conversion	Di/mono-alkylated ratio
Untreated	10.0	0.38	11.8	0.52
ETS (0.5)	8.7	0.55	24.2	0.70
ETS (1.5)	15.9	0.53	36.8	0.66
HTS	15.4	0.51	37.1	0.83
OTS	20.0	0.57	97.0	1.47

Table 4

Kinetics analysis of the m-cresol and 2-propanol reaction with the proposed reaction pathway.

Compound	Mole balance
Isopropanol (IPA)	$dC_{IPA}/dt = -k_1 C_{IPA}$
Propene (P)	$dC_P/dt = k_1 C_{IPA} - k_2 C_C C_P - k_3 C_{MONO} C_P - k_4 C_{DI} C_P$
m-Cresol (C)	$dC_C/dt = -k_2 C_C C_P$
Mono-alkylated products (MONO)	$dC_{MONO}/dt = k_2 C_C C_P - k_3 C_{MONO} C_P$
Di-alkylated products (DI)	$dC_{DI}/dt = k_3 C_{MONO} C_P - k_4 C_{DI} C_P$
Tri-alkylated products (TRI)	$dC_{TRI}/dt = k_4 C_{DI} C_P$
Polymerization products (OTHERS)	$dC_{OTHERS}/dt = k_5$

Deactivation function: $k_i = k_i^0 e^{-\tau}$ where τ is the deactivation parameter.

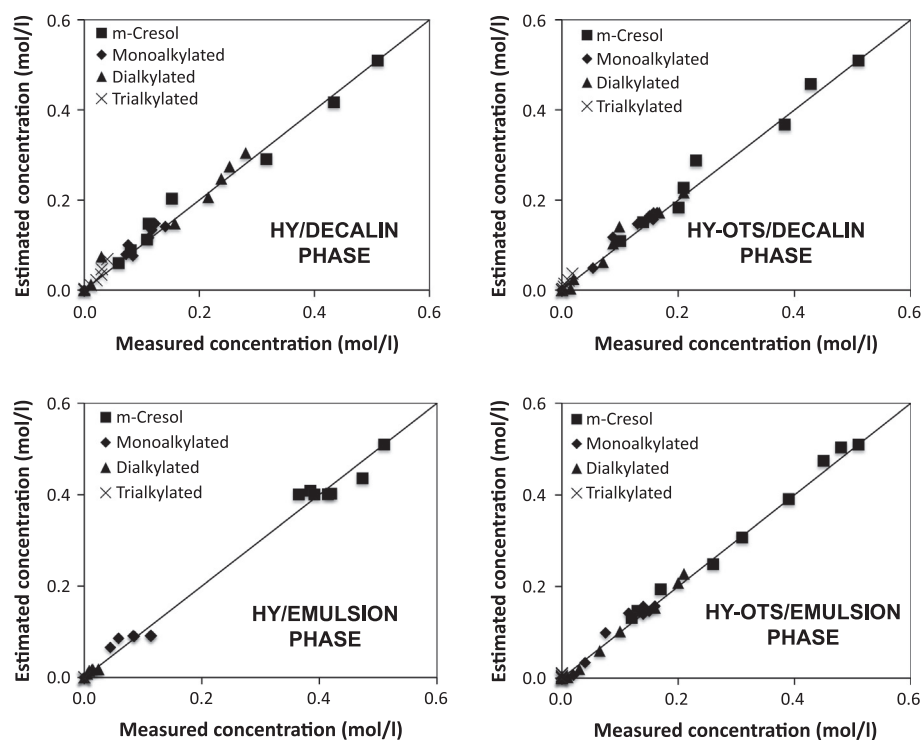


Fig. 19. Comparison of measured product and cresol concentrations and calculated concentrations based on the fittings using the simplified kinetics model described in Table 4 for the four cases investigated (catalysts: untreated and OTS-functionalized H-USY; solvents: decalin single phase and in water/decalin emulsion).

cases, water molecules do penetrate the zeolite structure and compete for adsorption sites with the reactants (isopropanol, propylene, cresols). This result is indeed expected, since regardless of the hydrophobicity of the external surface, the water coverage inside the zeolite crystal is given by the chemical potential of water, which in both cases is the same and in equilibrium with the partial pressure of water vapor above the liquid in the reactor, regardless whether the zeolite is wetted or not by liquid water.

On the other hand, an enormous difference is observed in the rate of deactivation of the two zeolites in the presence of water. Fig. 20 illustrates the deactivation functions predicted from the fitting for the four cases. It is clear that the untreated HY in the biphasic system is fully deactivated in about 3 h, while much lower deactivation is observed on the hydrophobized zeolite. This is the most important beneficial effect of the hydrophobic functionalization. By preventing the contact with liquid water, the silane groups

Table 5

Reaction and deactivation constants obtained at 200 °C and 700 psi of He over untreated and functionalized HY zeolite (Si/Al molar ratio: 30). Feed: isopropanol/m-cresol molar ratio: 4; total molar concentration: 2.5 M.

Rate constant/deactivation parameter	Decalin phase		Emulsion phase	
	HY	OTS-HY	HY	OTS-HY
k_1 (g cat ⁻¹ h ⁻¹)	17.3	11.7	2.63	0.96
k_2 (l g cat ⁻¹ mol ⁻¹ h ⁻¹)	7.26	5.22	1.23	0.26
k_3 (l g cat ⁻¹ mol ⁻¹ h ⁻¹)	11.2	6.15	1.83	0.35
k_4 (l g cat ⁻¹ mol ⁻¹ h ⁻¹)	1.44	1.26	0.20	0.02
k_5 (l ⁻¹ g cat ⁻¹ mol h ⁻¹)	0.23	0.22	0.03	0.01
τ (h ⁻¹)	0.10	0.10	1.50	0.09

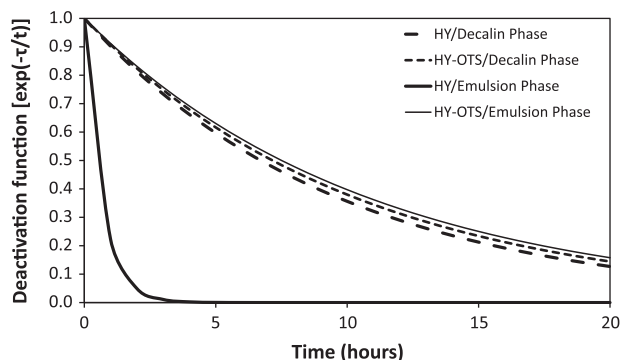


Fig. 20. Deactivation function resulting from the fitting of experimental data with the kinetic model described in Table 4, according to the expression $k_t = k_{t0} \exp(-\tau t)$, where k_t is the fitted reaction rate constants at $t = 0$ and τ is the deactivation parameter (see values in Table 4).

have preserved the zeolitic structure and therefore its catalytic activity. Indeed, the fitting shows that the rate of deactivation of the functionalized zeolite is essentially the same in decalin as in the emulsion, while the same is certainly not true for the untreated zeolite.

4. Conclusions

Several organosilanes of varying alkyl chain length (C2–C18) were examined as hydrophobizing agents of a commercial H-USY zeolite (Si/Al = 30). The structural tolerance of the various samples at 200 °C has been compared upon exposure to liquid reaction media (in biphasic emulsion) as well as increasing partial pressures of pure water vapor until a liquid phase is formed. Based on quantitative analysis that included N₂ physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and infrared spectroscopy (DRIFTS), the following explanation of the enhanced tolerance to hot liquid water upon hydrophobization can be proposed. The losses in zeolite crystallinity upon exposure to water at 200 °C are only significant when a condensed phase is in contact with the zeolite. Under these conditions, dissolution of crystals and mobility of ions are responsible of the attack. Therefore, zeolite deconstruction by hot liquid water is similar to the well-known zeolite recrystallization occurring under synthesis conditions. This interpretation is supported by experiments in which the chemical potential was kept constant while the amount of condensed water was increased. In those cases, the extent of zeolite destruction was significantly increased. Accordingly, the role of the hydrophobization with organosilanes is to prevent a direct contact of the zeolite with condensed water. The most effective hydrophobization to prevent collapse in the presence of pure water is one with high enough concentration of short alkyl-length organosilanes (e.g.,

ETS1.5) to reach all the defects and small pockets in the zeolite. By contrast, stability in biphasic water/oil systems is enhanced with long-alkyl chain silanes (e.g., OTS), which may enhance the interaction of the hydrophobized zeolite with the organic solvent that further protects it against the attack by water.

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Appendix A. Supplementary material

More details about nitrogen physisorption to determine micro and mesoporosity, XRD analysis to evaluate crystallinity, thermogravimetric analysis of functionalized samples, kinetics analysis and fitting, measurement of contact angle to determine hydrophobicity, and preparation of particle-stabilized emulsions are available in the Supporting Information file. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2013.05.024>.

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